

SCIENCE FOR GLASS PRODUCTION

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ON COLOR CENTERS IN GLASSES

Yu. A. Guloyan¹

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Materials for the most widely used colored glasses are analyzed according to types of coloring and color centers. Selenium coloring of glass is examined in greater detail from the standpoint of the current understanding of the structure of pigments and the formation of color centers. A more precise classification of the types of coloring and color centers in glasses is presented.

Key words: coloring, color centers: ionic, colloidal, molecular, and radiation.

Articles made of colored glass have an important place in overall glass production. At the same time coloring compounds are important in colored glass and glassware technology. Obsolete terminology, pertaining to the molecular nature of coloring, is not in keeping with our current understanding of the nature of coloring but is still used in widely read textbooks and technical literature on glass technology. Thus, there is a need to refine certain information pertaining to color centers in glasses taking account of our current scientific understanding.

First, it should be noted that definite structural elements or their combinations are responsible for the color of glass. The molecular concepts published at the end of the 19th century were some of the first scientific representations of the structure of natural silicate melts, metallurgical slag, and glass [1, 2]. According to these concepts the chemical compounds entering into the composition of complex silicates are present as molecules in them.

Subsequently, these ideas were changed as methods of investigation were developed and experimental data accumulated. It was shown that the compounds present in fused and solid silicate compounds are of ionic and not molecular nature.

Initially, the structural approach to colored glass was also identified with the existence of molecules of coloring compounds. This approach survived for quite a long time. Pigments were divided into molecular (solutes in melt) and colloidal (existing as colloidal particles in melt) [3, 4]. At the

same time extensive experimental and theoretical data, systematized in the monograph [5], were discussed from the ionic standpoint.

The advances made in colloidal and coordination chemistry, the chemistry of inorganic polymers, and the foundations of nanotechnologies as well as the results obtained in theoretical and experimental research now make it possible to construct a more accurate classification of the types of coloring and color centers in glass.

Ionic Color Centers. These color centers form in glass when transition and rare-earth metals are used. Current ideas link coloring to the formation of coordination (complex) compounds in which the character of the chemical bond is considered from the standpoint of ligand field theory. The basic assumptions and methods adopted in this theory make it possible to calculate quite accurately the spectral characteristics of color complexes, including for glasses [6, 7].

Coloring characteristics are determined by electronic-vibrational interactions in coordination polyhedra under exposure to light radiation.

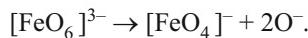
The activity of transition and rare-earth metal compounds is determined by the following:

- the nature of the ion (size, charge, electronic configuration, polarizability, and so on);
- type and properties of the ligands in a coordination polyhedron;
- the coordination number and symmetry of the coordination polyhedron;
- redox interactions;
- temperature conditions.

¹ Scientific–Research Institute of Glass, Gus’-Khrustal’nyi, Russia (e-mail: yu_guloyan@mail.ru).

The character of amber coloring of glass, widely used in the production of glass containers, is worth noting. In the past this type of coloring was attributed to the formation of molecular color centers, specifically, FeS and polysulfides. But research has shown that amber color is due to a tetrahedral coordination complex consisting of Fe^{3+} with three oxygen ions and one S^{2-} ion [8 – 10].

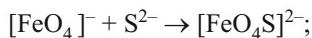
The process that results in the formation of an amber chromophore is quite complicated. When a high-temperature glass-forming melt is formed, many active oxygen ions and considerably fewer S^{2-} ions appear in it. The chemical affinity of Fe^{2+} ions to oxygen is much higher than to sulfur, as a result of which primarily complexes of Fe^{3+} with oxygen ligands will form. At the same time, at high temperatures and when the bonds formed are energy-nonequivalent partial dissociation of oxygen complexes of Fe^{3+} with a change of the coordination number and formation of unstable reactive complexes $[\text{FeO}_4]^-$ occurs:



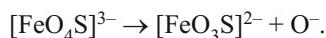
As a result of the presence of S^{2-} ions in the melt the oxygen ligands bind into SO_2 molecules: $2\text{O}^- + \text{S}^{2-} \rightarrow \text{SO}_2$.

Subsequently, the reaction proceeds by the ligand-substitution mechanism:

1) formation of an intermediate with a high coordination number:



2) rearrangement of the intermediate by matching ligand transference:



The detached oxygen ligands interact with S^{2-} and Na^+ ions present in the melt, forming SO_2 molecules and cationic structural fragments: $2\text{O}^- + \text{S}^{2-} \rightarrow \text{SO}_2$; $\text{O}^- + 2\text{Na}^+ \leftrightarrow \text{Na}_2\text{O}$.

The quite high intensity of the coloring is explained by absorption in the high-energy UV range, the violet range of the visible spectrum close to it, and charge transfer. This imparts good light-protection properties to glass used for containers storing foods and medicines.

Disperse Color Centers. These color centers in transparent, opalescent, and opacified glasses appear during the formation of metallic and non-metallic crystals and nanocrystals. Opacification is considered to be a type of coloring.

The coloring characteristics are determined by optical phenomena when light interacts with metallic and non-metallic (semiconducting) particles.

The size classification adopted in colloidal chemistry for disperse systems is fully applicable for transparent colored, opalescent, and opacified glass. This classification divides disperse systems into three groups with approximate size limits:

1) colloidal (particle size $10^{-8} - 10^{-7}$ m);

2) microheterogeneous (particle size $10^{-7} - 10^{-5}$ m);

3) coarsely disperse (particle size $(0.5 - 1.5) \times 10^{-3}$ m).

Glasses colored by nanocrystals of metals and nonmetals (yellow and ruby glass, surface-colored float-glass, and others) belong to the first group, opalescent and opacified (opacification by fluorides, phosphates, sulfides, and so forth) to the second group, and aventurine (copper and chromium) to the third group.

The color of glass with disperse color centers is determined by the interaction of the light flux with the disperse particles.

The color of metallic nanoparticles depends on the absorption and scattering conditions and is a function of the particle size.

For nonmetallic coloring nanoparticles glass color is determined by the color of the disperse phase, whose transmission is selective; particle size is less important. When nonmetallic particles opacify glass the character of the opacification depends on the scattering of the light flux. For coarsely disperse particles (crystals) the aventurine effect in glass is determined by the absorption, scattering, and reflection of the light flux. The conditions for colloidal coloring of glass are examined in greater detail in [11] taking account of the elements of nanotechnologies.

Molecular Color Centers. The most common types of coloring are ionic and disperse. Molecular color centers can form when pigments associated with inorganic chain molecules are used. Such polymers contain molecular chains in which the atoms are bound by rigid covalent bonds and the intermolecular bonds are much weaker.

Selenium is a characteristic example of such inorganic polymers. Below, the particulars of the structure of selenium as a pigment will be examined and the character of the glass color when obtaining "selenium rosaline" glass will be specified more precisely. This type of coloring is used comparatively rarely and is applied in the production of house ware and decorative glass articles. A quite detailed review of work along this line is given in W. Weyl's monograph [5]. It has been concluded on the basis of correlation of the results of series of studies, specifically, those by R. Lorenz and W. Aytel (1926), that the color is due to the formation of a "pyrosol" — an atomic solution of selenium in glass. This conclusion is made by analogy with solutions of metals in glass, which form a kind of "frozen metallic vapor."

In recent years, new information has appeared about the structure of the coloring substances and the character of the coloring of glass and an approach to technological processes with participation of nanoparticles and so forth has been under development.

Elemental selenium exists in two modifications: crystalline and amorphous. In either modification selenium is a homochain inorganic polymer. Thermodynamically stable crystalline gray selenium has been studied in greatest detail. This is a polymer with screw-shaped macromolecules packed parallel to one another. The atoms in the atomic chains are bound covalently, while the chain molecules are

bound by molecular forces and, in part, by a metallic bond. As for amorphous selenium, it is also a polymer with a chain structure but the degree of structural order is low. The configuration of the outer electronic shell of the selenium atom is $4s^24p^4$; the spins two of the p-electrons are paired while the spins in the other two are not paired. As a result, the selenium atoms can form Se_2 molecules or chains of atoms Se_n . The chains of atoms can close into ring molecules, for example, Se_8 . The diversity of molecular structure makes it possible for selenium to exist in different allotropic modifications: crystalline (monoclinic α , β forms and hexagonal γ form) and amorphous (powder, colloidal, and glassy). The hexagonal γ form has a gray color, the monoclinic α and β forms are red, the amorphous modifications (powder and colloidal) are red, and the glassy modification is black with a red tinge (in transmission).

Even fused or dissolved selenium does not "separate" into individual atoms. Atomic-molecular chains of different length and ring formations, for example, eight-member rings Se_8 , are preserved when selenium fuses and dissolves. Structural combinations occurring in larger numbers also exist. Even gaseous selenium exists in the form of separate atoms only at temperatures above $1500^\circ C$. At lower temperatures selenium exists in the form of two-, six- and eight-member linear and closed chains. Molecules with the composition Se_6 predominate up to $900^\circ C$ and Se_2 above $1000^\circ C$ [12].

In summary, strong covalent bonds in selenium molecules preserve the molecular structure of selenium in melt and solid glass. Since all amorphous modifications of selenium are red, it can be assumed that when "selenium rosoline" is obtained the color centers are of a molecular na-

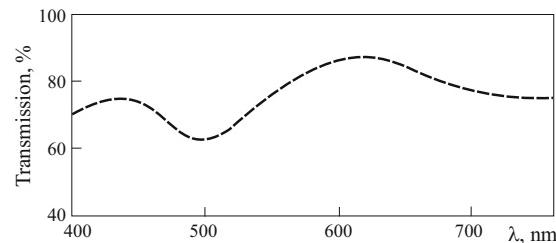


Fig. 1. Spectral transmission of "selenium rosoline."

ture. In glass, color centers exist in the form of molecular clusters — molecular formations with average characteristic size to 10 nm. The fundamentals of the physical chemistry of cluster formation are presented in [13].

When selenium rosoline glasses are made the selenium introduced into the batch rapidly volatilizes (sublimates). The losses are 70 – 80% of the selenium introduced; colorless alkali-metal chemical compounds (selenites and selenates) form and undergo thermal dissociation as temperature increases. As a result, only 0.02 – 0.05% Se remains in the glass. Increasing the amount of selenium or its compounds introduced does not deepen the rose color [14, 15]. The spectral transmission of "selenium rosoline" is shown in Fig. 1 (Se content in glass 0.03%, sample thickness 10 mm) [15]. The color is due to two absorption bands: 500 and 750 nm. As temperature increases, the bands broaden and shift in the direction of longer wavelengths and a yellowish-brown tinge appears; as temperature decreases, the yellowish-brown tinge disappears.

TABLE 1. Types of Coloring and Color Centers and Their Characteristics

Types of coloring	Color centers	Coloring character
Ionic	Complexes of transition and rare-earth metals with oxygen and sulfur-oxygen* ligands (octahedral and tetrahedral coordination) — all forms of commercial glass	Electronic-vibrational interactions in coordination polyhedra
Disperse	Crystals and nanocrystals of metals and nonmetals	Optical phenomena due to interaction of light with disperse particles
Colloidal Particle size $10^{-8} - 10^{-7}$ m	Nanocrystals of metals and nonmetals (semiconductors) — transparent color centers	<i>Nanocrystals of metals</i> — absorption, scattering <i>Nanocrystals of nonmetals</i> — selective transmission
Microheterogeneous Particle size $10^{-7} - 10^{-5}$ m	Crystals of metals and nonmetals — opalescent and opacified systems	Scattering
Coarsely disperse Particle size $(0.5 - 1.5) \times 10^{-3}$ m	Crystals of metals (Cu) and nonmetals (Cr_2O_3) — aventurine glass	Absorption, scattering, reflection
Molecular	Selenium molecules and molecular clusters — selenium-colored glass	Electronic-vibrational interactions in molecular structures
Radiation	Structural defects, free electrons (high-energy radiation) Coloring ionic complexes, colloidal particles of metals (UV radiation) — photochromic, uviolet glass, and others	Quantum-electronic interactions Photochemical interactions (solarization, photochromism, and so forth)

* Amber and brown color $[FeO_3S]^{2-}$.

The results of modeling the properties of bulk objects by analyzing the properties of selenium nanoclusters are presented in [16]. This theoretical technique has been used successfully in a number works to analyze the properties and structure of crystalline and amorphous materials. Summarizing the data of [16], it can be assumed that the basic elements of the electronic and vibrational structure of Se are already present in a 10 Å cluster and therefore the Se structure can be regarded as a collection of the clusters mentioned above. Thus, taking account of the strong bonds between selenium atoms, we obtain in a glass-forming melt containing elemental selenium a complex of molecular clusters of selenium with atomic chains of different length (ranging from Se_2 to Se_8). As temperature decreases, polymerization and a transition from short linear molecular chains (Se_2) to longer chains and molecular rings (Se_8), giving a red color, occur. Since the selenium concentration in the melt is low, we obtain glass with a weak rose color.

Radiation Color Centers. When glass is exposed to high-energy ionizing radiation (x-rays, γ -rays, and neutrons) the equilibrium in the atomic-electronic subsystem is disrupted: this subsystem is transferred into an excited state and free electrons and valence-unsaturated coordination groups appear with structural defects arising in consequence. Free electrons are captured by different structural defects and corresponding color centers capable of absorbing visible-range radiation are formed. The absorption spectrum is complicated. Brown hues due to the superposition of bands from different color centers predominate in it.

Ultraviolet radiation also falls into this group but its effect is much weaker. Solarization phenomena, the aging of uviol glass, and photochromism are associated with UV radiation.

The subsystem's return to equilibrium, which is associated with the destruction of color centers and weakening and vanishing of color, is effectuated by relaxation phenomena, which can be accelerated by thermal and optical stimulation [17, 18].

A more precise classification color types and centers was devised on this basis and is presented in Table 1.

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